

CHEMICAL SOLUTION  
FOR ELECTROPLATING A COPPER-ZINC ALLOY THIN FILM

CROSS-REFERENCE TO RELATED APPLICATION(S)

**[0001]** This application is also related to the following commonly assigned applications, entitled:

- (1) "Method of Electroplating a Copper-Zinc Alloy Thin Film on a Copper Surface Using a Chemical Solution and a Semiconductor Device thereby Formed," concurrently filed (S/N to be assigned);
- (2) "Method of Controlling Zinc-Doping in a Copper-Zinc Alloy Thin Film Electroplated on a Copper Surface and a Semiconductor Device thereby Formed," concurrently filed (S/N to be assigned);
- (3) "Method of Reducing Electromigration in a Copper Line by Electroplating an Interim Copper-Zinc Alloy Thin Film on a Copper Surface Using a Chemical Solution and a Semiconductor Device thereby Formed," concurrently filed (S/N to be assigned);
- (4) "Method of Reducing Electromigration in a Copper Line by Zinc-Doping of a Copper Surface from an Electroplated Copper-Zinc Alloy Thin Film and a Semiconductor Device thereby Formed," filed on December 7, 2001, U.S. Patent Application Serial No. 10/016,410;
- (5) "Method of Reducing Electromigration by Forming an Electroplated Copper-Zinc Interconnect and a Semiconductor Device thereby Formed," concurrently filed (S/N to be assigned); and
- (6) "Method of Reducing Electromigration by Ordering Zinc-Doping in an Electroplated Copper-Zinc Interconnect and a Semiconductor Device thereby Formed," filed on December 7, 2001, U.S. Patent Application Serial No. 10/016,645.

TECHNICAL FIELD

**[0002]** The present invention relates to semiconductor devices and their methods of fabrication. More particularly, the present invention relates to the processing of copper interconnect material and the resultant device utilizing the same. Even more particularly, the present invention relates to reducing electromigration in copper interconnect lines by doping their surfaces with a barrier material using wet chemical methods.

## BACKGROUND ART

[0003] Currently, the semiconductor industry is demanding faster and denser devices (e.g., 0.05- $\mu\text{m}$  to 0.25- $\mu\text{m}$ ) which implies an ongoing need for low resistance metallization. Such need has sparked research into resistance reduction through the use of barrier metals, stacks, and refractory metals. Despite aluminum's (Al) adequate resistance, other Al properties render it less desirable as a candidate for these higher density devices, especially with respect to its deposition into plug regions having a high aspect ratio cross-sectional area. Thus, research into the use of copper as an interconnect material has been revisited, copper being advantageous as a superior electrical conductor, providing better wettability, providing adequate electromigration resistance, and permitting lower depositional temperatures. The copper (Cu) interconnect material may be deposited by chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD), sputtering, electroless plating, and electrolytic plating.

[0004] However, some disadvantages of using Cu as an interconnect material include etching problems, corrosion, and diffusion into silicon.<sup>1</sup> These problems have instigated further research into the formulation of barrier materials for preventing electromigration in both Al and Cu interconnect lines. In response to electromigration concerns relating to the fabrication of semiconductor devices particularly having aluminum-copper alloy interconnect lines, the industry has been investigating the use of various barrier materials such as titanium-tungsten (TiW) and titanium nitride (TiN) layers as well as refractory metals such as titanium (Ti), tungsten (W), tantalum (Ta), molybdenum (Mo), and their silicides.<sup>2</sup> Although the foregoing materials are adequate for Al interconnects and Al-Cu alloy interconnects, they have not been entirely effective with respect to all-Cu interconnects. Further, though CVD and PECVD have been conventionally used for depositing secondary metal(s) on a primary metal interconnect surface, neither technique provides a cost-effective method of forming a copper-zinc alloy on a Cu interconnect surface. Therefore, a need exists for a low cost and high throughput method of forming by

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<sup>1</sup>Peter Van Zant, Microchip Fabrication: A Practical Guide to Semiconductor Processing, 3<sup>rd</sup> Ed., p. 397 (1997).

<sup>2</sup>*Id.*, at 392.

electroplating a copper-zinc alloy (Cu-Zn) thin film on a copper (Cu) surface in a stable chemical solution which improves interconnect reliability, enhances electromigration resistance, and improves corrosion resistance.

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## DISCLOSURE OF INVENTION

[0005] Accordingly, the present invention provides a method for forming, by electroplating, a Cu-Zn alloy thin film on a Cu surface by electroplating the Cu surface in a unique nontoxic aqueous chemical electroplating solution containing salts of zinc (Zn) and copper (Cu), their complexing agents, a pH adjuster, and surfactants; and a semiconductor device thereby formed. The present invention further provides a particular electroplating method which controls the parameters of Zn concentration, pH, temperature, and time in order to form a uniform Cu-Zn alloy thin film for reducing electromigration in Cu interconnect lines by decreasing the drift velocity therein which decreases the Cu migration rate in addition to decreasing the void formation rate.

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[0006] More specifically, the present invention provides a method for fabricating a semiconductor device having a Cu-Zn alloy thin film formed on a Cu surface by electroplating the Cu surface in the present chemical solution. The method generally comprises the steps of: (1) providing a semiconductor substrate having a Cu surface; (2) providing a chemical solution; (3) electroplating the Cu surface in the chemical solution, thereby forming the Cu-Zn alloy thin film on the Cu surface; (4) rinsing the Cu-Zn alloy thin film; (5) drying the Cu-Zn alloy thin film; and (6) completing fabrication of the semiconductor device.

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[0007] By electroplating this Cu-Zn alloy thin film on the Cu surface using a stable chemical solution in the prescribed concentration ranges, the present invention improves Cu interconnect reliability, enhances electromigration resistance, improves corrosion resistance, and reduces manufacturing costs. In particular, the present invention chemical solution is advantageous in that it facilitates formation of an acceptable Cu-Zn alloy thin film over a wide range of bath compositions. The desirable Zn concentration in the Cu-Zn alloy thin film, preferably in a range of approximately 0.2 at. % to approximately 9.0 at. % determined by X-Ray Photoelectron Spectroscopy (XPS) or Auger Electron Spectroscopy (AES), is controllable by varying the electroplating conditions and/or the bath composition.

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[0008] These advantages arise from the present invention's superior fill-characteristics.

The present Cu-Zn electroplating solution facilitates better filling of a Cu-Zn alloy thin film on an interconnect, especially for feature sizes in a dimensional range of approximately 0.2  $\mu\text{m}$  to approximately 0.05  $\mu\text{m}$ , thereby lowering the resistance of the formed Cu-Zn alloy thin film (e.g., in a resistance range of approximately 2.2  $\mu\Omega\cdot\text{cm}$  to approximately 2.5  $\mu\Omega\cdot\text{cm}$  for approximately 1 at. % Zn content in a Cu-Zn alloy thin film, as deposited).

Further, the filling capability is enhanced by three beneficial characteristics of the present invention: (1) the instant chemical solution does not etch copper or a copper alloy seed layer; (2) the introduction of Zn into the alloy thin film as well as onto the Cu interconnect improves both step coverage and nucleation; and (3) a variety of organic additives, such as polyethylene glycol (PEG), organo-disulfides, and organo-chlorides, are compatible and may be included in the instant chemical solution for further enhancing the fill profile and grain structure. The present Cu-Zn electroplating solution provides a desirably low Zn content in a Cu alloy interconnect (e.g., in a concentration range of approximately 0.2 at. % to approximately 1.0 at. %) which also imparts (1) a de minimis increase in resistance as well as (2) a maximum improvement in electromigration resistance. The present chemical solution can also provides a desirably low Zn content (e.g., in a range of  $<$  approximately 0.1 at. % or  $<<$  approximately 0.2 at. %, virtually undetectable by AES) in a Cu film, wherein the Zn content may be engineered by varying the deposition parameters as well as by modifying the bath composition.

#### BRIEF DESCRIPTION OF THE DRAWING(S)

[0009] For a better understanding of the present invention, reference is made to the below-referenced accompanying drawings. Reference numbers refer to the same or equivalent parts of the present invention throughout the several figures of the drawings.

- (1) Figure 1 is a cross-sectional view of a semiconductor device comprising a Cu-Zn alloy thin film deposited and disposed on a Cu surface, in accordance with the present invention.
- (2) Figure 2 is a flowchart of a method for synthesizing a unique nontoxic aqueous Cu-Zn electroplating (chemical) solution, in accordance with the present invention.
- (3) Figure 3 is a flowchart of a method for forming a Cu-Zn alloy thin film on a Cu surface, in accordance with the present invention.

## MODES FOR CARRYING OUT THE INVENTION

[0010] Figure 1 illustrates, by example only, and in cross-section, a Cu surface 20 having a Cu-Zn alloy thin film 30 thereon deposited, in accordance with the present invention.

[0011] Figure 2 flowcharts, by example only, a method M1 for synthesizing a liter of a unique nontoxic aqueous Cu-Zn electroplating (chemical) solution, in accordance with the present invention:

- (1) cleaning a mixing vessel (e.g., a beaker) with dilute nitric acid ( $\text{HNO}_3$ ) for approximately 5 minutes, as indicated by block 1001;
- (2) rinsing the mixing vessel in deionized (DI) water for approximately 5 minutes to approximately 10 minutes and subsequently drying the mixing vessel, for instance, under a gaseous nitrogen ( $\text{GN}_2$ ) flow, as indicated by block 1002;
- (3) adding an initial volume of DI water (e.g., approximately 400 ml) to the mixing vessel, as indicated by block 1003;
- (4) adding at least one Cu ion source for providing a plurality of Cu ions and stirring the at least one Cu ion source into the DI water for a duration in a range of approximately 5 minutes to approximately 10 minutes or until complete dissolution of the at least one Cu ion source in the DI water is achieved, as indicated by block 1004;
- (5) adding at least one complexing agent for complexing the plurality of Cu ions and stirring the at least one complexing agent until complete dissolution of the at least one complexing agent in the DI water is achieved, as indicated by block 1005;
- (6) adding at least one pH adjuster and stirring the at least one pH adjuster into the DI water for a duration in a range of approximately 5 minutes to approximately 10 minutes or until a clean and transparent solution is achieved, as indicated by block 1006;
- (7) measuring the pH of the solution, and, if the pH is within the desired range, proceeding to step (8), otherwise titrating the solution with a small volume of the at least one pH adjuster until the pH falls within the desired range, in essence, returning to step (6), as indicated by block 1007;
- (8) adding at least one Zn ion source for providing a plurality of Zn ions and stirring the at least one Zn ion source into the DI water for a duration in a range of approximately 5 minutes to approximately 10 minutes or until complete dissolution of the at least one Zn ion source in the DI water is achieved, as indicated by block 1008;

- (9) adding a final volume of DI water (e.g., effecting approximately 1 L in total solution volume) to the mixing vessel, as indicated by block 1009;
- (10) optionally adding at least one complexing agent for complexing the plurality of Zn ions and stirring the at least one complexing agent until complete dissolution of the at least one complexing agent in the DI water is achieved, as indicated by block 1010; and
- (11) measuring the pH of the solution, and, if the pH is within the desired range, terminating the synthesis, otherwise further titrating the solution with a small volume of the at least one pH adjuster until the pH falls within the desired range, in essence, returning to step (10), as indicated by block 1011.

**[0012]** In addition, the present invention chemical solution may be formulated as follows:

wherein the at least one zinc (Zn) ion source comprises at least one zinc salt selected from a group consisting essentially of zinc acetate  $((\text{CH}_3\text{CO}_2)_2\text{Zn})$ , zinc bromide  $(\text{ZnBr}_2)$ , zinc carbonate hydroxide  $(\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2)$ , zinc dichloride  $(\text{ZnCl}_2)$ , zinc citrate  $((\text{O}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2)\text{CH}_2\text{CO}_2)_2\text{Zn}_3)$ , zinc iodide  $(\text{ZnI}_2)$ , zinc L-lactate  $((\text{CH}_3\text{CH}(\text{OH})\text{CO}_2)_2\text{Zn})$ , zinc nitrate  $(\text{Zn}(\text{NO}_3)_2)$ , zinc stearate  $((\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2)_2\text{Zn})$ , zinc sulfate  $(\text{ZnSO}_4)$ , zinc sulfide  $(\text{ZnS})$ , and zinc sulfite  $(\text{ZnSO}_3)$ , and their hydrates (preferably zinc chloride or zinc dichloride and zinc citrate), wherein the at least one complexing agent for complexing the plurality of Zn ions comprises tartaric acid  $(\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H})$ , wherein the tartaric acid prevents precipitation of the plurality of Zn ions from the chemical solution, wherein the at least one copper (Cu) ion source comprises at least one copper salt selected from a group consisting essentially of copper(I) acetate  $(\text{CH}_3\text{CO}_2\text{Cu})$ , copper(II) acetate  $((\text{CH}_3\text{CO}_2)_2\text{Cu})$ , copper(I) bromide  $(\text{CuBr})$ , copper(II) bromide  $(\text{CuBr}_2)$ , copper(II) hydroxide  $(\text{Cu}(\text{OH})_2)$ , copper(II) hydroxide phosphate  $(\text{Cu}_2(\text{OH})\text{PO}_4)$ , copper(I) iodide  $(\text{CuI})$ , copper(II) nitrate hydrate  $((\text{CuNO}_3)_2)$ , copper(II) sulfate  $(\text{CuSO}_4)$ , copper(I) sulfide  $(\text{Cu}_2\text{S})$ , copper(II) sulfide  $(\text{CuS})$ , copper(II) tartrate  $((\text{CH}(\text{OH})\text{CO}_2)_2\text{Cu})$ , and their hydrates (preferably copper sulfate), wherein the at least one complexing agent for the plurality of Cu ions comprises at least one species selected from a group consisting essentially of ethylene diamine "EDA"  $(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)$  and ethylenediaminetetraacetic acid "EDTA"  $((\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2)$ , wherein the at least one complexing agent for the plurality of Cu ions prevents precipitation

of the plurality of Cu ions from the chemical solution, wherein the at least one pH adjuster comprises at least one pH-adjusting compound selected from a group consisting essentially of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and tetramethylammonium hydroxide "TMAH" ( $(\text{CH}_3)_4\text{NOH}$ ), wherein the at least one wetting agent comprises a surfactant, and wherein the surfactant comprises at least one surfactant selected from a group consisting essentially of RE-610™ and polyethylene glycol (PEG).

[0013] In the preferred embodiment of the chemical solution, the composition in the method M1 is formulated with component concentration ranges as follows: wherein the at least one zinc (Zn) ion source is provided in a concentration range of approximately 5 g/L to approximately 25 g/L (preferably approximately 10 g/L), wherein the at least one complexing agent for complexing the plurality of Zn ions is provided in a concentration range of approximately 10 g/L to approximately 30 g/L (preferably approximately 20 g/L), wherein the at least one copper (Cu) ion source is provided in a concentration range of approximately 5 g/L to approximately 25 g/L (preferably approximately 10 g/L), wherein the at least one complexing agent for complexing the plurality of Cu ions is provided in a concentration range of approximately 40 g/L to approximately 100 g/L (preferably approximately 80 g/L), wherein the at least one pH adjuster is provided in a concentration range of approximately 10 g/L to approximately 20 g/L (preferably approximately 15 g/L), wherein the at least one wetting agent is provided in a concentration range of approximately 0.01 g/L to approximately 0.1 g/L (preferably approximately 0.02 g/L), and wherein the volume of water is provided in a volume range of up to and including approximately 1 L.

[0014] Also, the preferred embodiment of the device fabrication involves the following process parameters ranges: wherein the at least one pH adjuster adjusts the chemical solution to a pH range of approximately 7.5 to approximately 14 (preferably in a pH range of approximately 10 to approximately 12), wherein the chemical solution may be maintained in a temperature range of approximately 16°C to approximately 35°C (preferably at a temperature of approximately 24°C), wherein the Cu surface 20 is electroplated for a duration in a range of approximately 15 seconds to approximately 120 seconds (preferably for a duration of approximately 60 sec), wherein the Cu-Zn alloy thin film 30 is formed having a thickness in a range of approximately 10 nm to approximately

200 nm (preferably having a thickness of approximately 30 nm), and wherein the formed Cu-Zn alloy thin film 30 has a de minimis Zn content in a concentration range of at least approximately 0.1 at. % to approximately 1 at. %.

[0015] Figure 3 flowcharts, by example only, a method M2 for forming a copper-zinc alloy (Cu-Zn) thin film 30 on a copper (Cu) surface 20, having been formed by chemical vapor deposition (CVD), plasma vapor deposition (PVD), plasma-enhanced vapor deposition (PECVD), or electroplating, by treating the Cu surface 20 in a chemical solution, comprising the steps of: (1) providing a semiconductor substrate having a Cu surface 20, as indicated by block 2001; (2) providing a chemical solution, the chemical solution comprising: at least one zinc (Zn) ion source for providing a plurality of Zn ions; at least one copper (Cu) ion source for providing a plurality of Cu ions; at least one complexing agent for complexing the plurality of Cu ions; at least one pH adjuster; at least one wetting agent for stabilizing the chemical solution, all being dissolved in a volume of water, as shown by block 2002; (3) electroplating the Cu surface 20 in the chemical solution, thereby forming the Cu-Zn alloy thin film 30 on the Cu surface 20, as shown by block 2003; (4) rinsing the Cu-Zn alloy thin film 30 formed on the Cu surface 20 in water, as shown by block 2004; (5) drying the Cu-Zn alloy thin film 30 formed on the Cu surface 20, for instance, under a gaseous nitrogen flow ( $\text{GN}_2$ ), as shown by block 2005; and (6) completing fabrication of the semiconductor device, as shown by block 2006. The chemical solution may optionally further comprise at least one complexing agent for complexing the plurality of Zn ions.

[0016] Information as herein shown and described in detail is fully capable of attaining the above-described object of the invention, the presently preferred embodiment of the invention, and is, thus, representative of the subject matter which is broadly contemplated by the present invention. The scope of the present invention fully encompasses other embodiments which may become obvious to those skilled in the art, and is to be limited, accordingly, by nothing other than the appended claims, wherein reference to an element in the singular is not intended to mean "one and only one" unless explicitly so stated, but rather "one or more." All structural and functional equivalents to the elements of the above-described preferred embodiment and additional embodiments that are known to those of ordinary skill in the art are hereby expressly incorporated by reference and are intended to be encompassed by the present claims.



[0017] Moreover, no requirement exists for a device or method to address each and every problem sought to be resolved by the present invention, for such to be encompassed by the present claims. Furthermore, no element, component, or method step in the present disclosure is intended to be dedicated to the public regardless of whether the element, component, or method step is explicitly recited in the claims. However, it should be readily apparent to those of ordinary skill in the art that various changes and modifications in form, semiconductor material, and fabrication material detail may be made without departing from the spirit and scope of the inventions as set forth in the appended claims. No claim herein is to be construed under the provisions of 35 U.S.C. §112, sixth paragraph, unless the element is expressly recited using the phrase "means for."

#### INDUSTRIAL APPLICABILITY

[0018] The present invention relates to reducing electromigration in copper interconnect lines by doping their surfaces with a barrier material using wet chemical methods in the semiconductor fabrication industry. In particular, the present invention provides a method for forming, by electroplating, a Cu-Zn alloy thin film on a Cu surface by electroplating the Cu surface in a unique nontoxic aqueous chemical electroplating solution containing salts of zinc (Zn) and copper (Cu), their complexing agents, a pH adjuster, and surfactants; and a semiconductor device thereby formed. The present invention further provides a specific electroplating method which controls the parameters of Zn concentration, pH, temperature, and time in order to form a uniform Cu-Zn alloy thin film for reducing electromigration in Cu interconnect lines by decreasing the drift velocity therein which decreases the Cu migration rate in addition to decreasing the void formation rate in semiconductor device Cu lines.